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MONITORING THERMAL PROPERTIES OF VARIOUS LDPE/POLYSACCHARIDES BLENDS

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ABSTRACT: Polymers, which are currently biodegradable, capture high interest in materials science since they offer reductions of ladfill space during waste management, as well as new end-user benefits in various fields of applications [1]. The greatest application of polysaccharides, especially xylans or starch and its derivatives in the polymers field, is their use as components in various polymer formulations [2-4]. Most of the applications are focused on polyethylene, which is widely used as packaging material [5]. This article deals with blends preparation of low density polyethylene (LDPE) and lauroylated glucuronoxylan Lenzing (LaCOLX) with DS = 1.9, lauroylated carboxymethylstarch [6] and carboxymethylstarch (CMS) with DS = 0.3 in different amounts, with and without compatibilizer (poly(ethylene-co-acrylic) acid copolymer (EAA)). This type of compatibilizer was used at the preparation of LDPE/polysaccharide blends described in [7]. Thermal analysis of LDPE/polysaccharides blends with different polysaccharide content, were performed by TGA [8,9]. From the TGA analysis, we concluded that the thermal stability of the compatible blends was higher than the one of incompatible blends. This can be due to presence of EAA, which can increase the thermal stability of LDPE/polysaccharides blends.

KEY WORDS: TGA, Thermal stability, LDPE, glucuronoxylans, carboxymethylstarch

1. INTRODUCTION

Polymers in the environment undergo gradual decomposition due to the effect of different factors, e.g. light, moisture, air, temperature, wind and macro- and/or microorganisms. Biodegradation follows photodegradation and chemical degradation most frequently. Unmodified polyolefines are resistant to biodegradation, but when filled with polysaccharides – natural polymers – they are counted among the biodegradation susceptible polymers [10]. Natural polymers are a complex mix of organic materials and, as a result of that, thermal treatment produces a variety of chemical and physical changes. Polymer or polymer blend stability can be studied by using TGA. TGA curves show one or two decomposition steps. Pyrolysis reaction of polysaccharides produces gases and follows first-order kinetics [11]. Thermal degradation of blends of synthetic polymers with natural polymers produces volatiles and composites with low density and lower mechanical properties [12]. Organoleptic properties as smell and colour increase when polysaccharides degrade. Another effect is the change of mechanical properties by mass and crystallinity changes and reduction of degree of polymerization due to chain breakage by glycosidic union decomposition producing carbon dioxide and water. All kinetic studies utilize the basic rate equation:

$$\frac{d\alpha}{dt} = k.f(\alpha) \qquad (1)$$

In the case of polymer degradation, it is assumed that the rate of conversion is proportional to the concentration of material that has to react:

$$f(\alpha) = (1-\alpha)^n \qquad (2)$$

The aim of the present work is to determine a global kinetic expression for the thermal degradation of the LDPE/polysaccharides blends, as well as the effect of the content of polysaccharide and compatibilizer EAA.

2. EXPERIMENT

Materials

The low density polyethylene (LDPE) (Slovnaft Petrochemicals) which we used was appropriate for packing application. Ethylene/acrylic acid copolymer (EAA) containing 15 wt.% acrylic acid was supplied from Aldrich. Carboxymethyl starch (CMS) with degree of substitution DS = 0.3 was prepared by reaction of potato starch (Jena) suspended in methanol with monochloracetic acid after the activation by 40 % aqueous sodium hydroxide. Carboxymethyl starch laurate (LaCMS) with DS = 2.45 was prepared by the reaction with lauroyl chloride [13]. Water-insoluble glucuronoxylan (LX), a by-product of viscose production from beech sulfite pulp, was a gift from Lenzing AG (Austria): Xyl = 92.5 % (of neutral sugars), MeGUA = 3.7 %, $Mw \sim 5000$ g/mol. Glucuronoxylan Lenzing laurate (LaCOLX) with DS = 1.9 was prepared by reaction with lauroyl chloride [13].

Melt-blending

Three different types of polysaccharides were melt-blended with LDPE in Brabender Plasti – Corder PLE 331. Mixing was performed at 140 °C and 80 rpm for 15 min. For LDPE/LaCMS and LDPE/CMS blends, four different levels of carboxymethyl starch were used, namely 5, 10, 15 and 20 wt.%. For LDPE/LaCOLX or LX blends, four different levels of LaCOLX were used, namely 1, 3, 5 and 10 wt.%. In LDPE/CMS and LDPE/LaCOLX blends EAA was used as a compatibilizer at three different amounts, namely 10, 25 and 50 wt.% based upon polysaccharide.

TGA Measurements

TGA measurements were performed in a Thermobalance Mettler Toledo TGA/SDTA 851e thermogravimetric analyzer. Measurements were performed under nitrogen atmosphere by using a heating rate of 10 °C/min up to 550 °C. Both the polysaccharide content and the thermal stability of the blends can be estimated from the weight loss.

3. RESULTS AND DISCUSSION

When starch granules are heated under atmospheric conditions, they are thermally stable up to 200 - 230 °C. Beyond 230 - 250 °C, thermal degradation takes place, depending mainly on the water content of the starch [14]. Thermal degradation could take place during the thermal processing of starch and especially during extrusion, resulting in the formation of lower molecular weight starch molecules. This could seriously affect mechanical properties of the final product. Colour development is another undesirable effect of degradation.

The stability of CMS is 245 - 260 °C. This good thermal stability of CMS compared to starch is probably due to the low content of hydroxyls in the former [15]. Fig. 1 presents the TGA thermograms of LDPE/CMS/EAA blends with presenting no significant differences compared to those of pure LDPE. The blends of LDPE with carboxymethyl starch showed two decomposition stages. The first one (271 - 360 °C) is due to carboxymethyl starch decomposition. The second stage, appearing at higher temperatures, is due to LDPE decomposition. TGA measurements of the blends of LaCMS with LDPE are shown in Tab 1. The first one (367 - 373 °C) is due to LaCMS decomposition and the second one appearing in higher temperatures (434 - 438 °C) is due to LDPE decomposition. The higher thermal stability of LaCMS is expected to minimise processing problem such as colour formation.

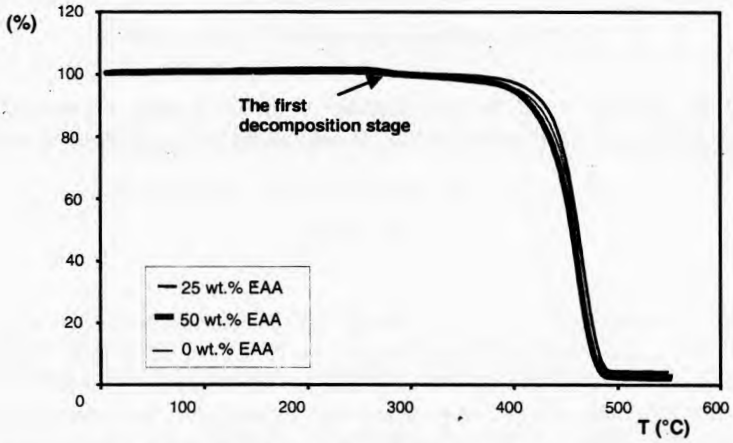

Fig. 1: TGA thermogram of LDPE/CMS blends with 5 wt.% CMS and different amounts of EAA

Tab. 1: Thermal properties of LDPE and LDPE/LaCMS blends with different amounts of LaCMS

Sample	T_{on1} (°C)	T_{on2} (°C)	Weight loss at 420 °C (%)	Weight loss at 550 °C (%)
LDPE	-	434.5	-	99.10
LDPE/1 wt.% LaCMS	-	435.4	-	99.16
LDPE/3 wt.% LaCMS	373.06	435.7	3.05	98.91
LDPE/5 wt.% LaCMS	367.68	438.4	4.67	99.30
LDPE/10 wt.% LaCMS	368.22	438.3	9.90	98.39

Glucuronoxylan LX is thermally stable up to 240 - 244 °C. By esterification of LX with acylchlorides it is possible to improve its thermal stability. This is due to low content of hydroxyl groups in the start xylan. Highly substituted glucuronoxylan was used in this study for preparation of LDPE blends with aim to increase thermal stability of blends.

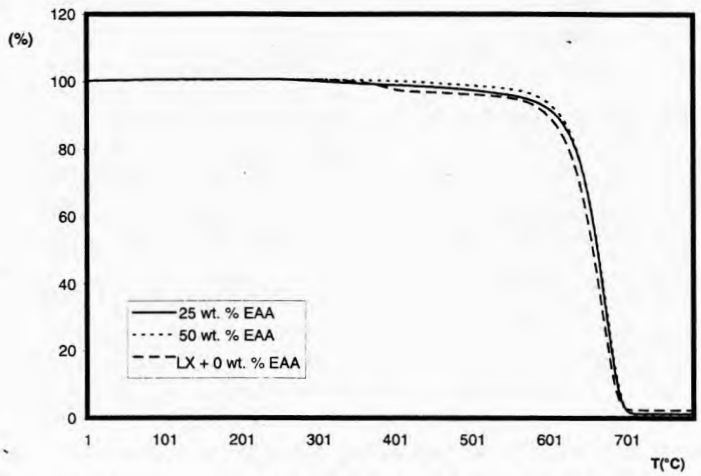

Fig. 2: TGA thermogram of LDPE/LaCOLX blends with 5 wt.% LaCOLX and different amounts of EAA

We can see from Fig. 2, that prepared LDPE blends with 5 wt.% of LaCOLX and different amount of EAA have good thermal stability. The decomposition of LaCOLX is 420 - 431 °C. The blends of LDPE with 5 wt.% of xylan Lenzing (LX) without EAA showed two decomposition stages.

The first one (348 - 401 °C) is due to LX decomposition, the second stage, appearing at higher temperatures, is due to LDPE decomposition. The compatibilized LDPE/LaCOLX blends have better thermal stability than uncompatibilized LDPE/LX blends (Fig. 2). This result also indicates that the compatibilizer EAA enhanced interfacial adhesion between LDPE and polysaccharide and there are molecular interactions between EAA and xylan Lenzing laurate (LaCOLX) in LDPE blends [3].

4. CONCLUSIONS

In this study, three types of polysaccharides were used in order to prepare blends with synthetic polymer – low density polyethylene. For advance of interfacial adhesion between synthetic polymer and polysaccharide, ethylene/acrylic acid copolymer was used as a compatibilizer. A series of LDPE/CMS, LDPE/LaCMS and LDPE/LaCOLX blends with or without compatibilizers (EAA), has been prepared and extensively studied for their thermal behavior. All prepared blends exhibit good thermal properties. It was found that the increase in polysaccharide content does not affect thermal stability of LDPE/polysaccharide blends. On the other hand, type of used polysaccharide affects thermal stability of blends. The compatibilized LDPE/LaCOLX blends had the best thermal stability of all prepared blends. TGA results indicate that there are molecular interactions between compatibilizer and polysaccharide in LDPE blends. The presence of EAA copolymer can improve the thermal stability of the blends.

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5. REFERENCES

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